CHAPTER 5

RESULTS AND DISCUSSION

Batch Kinetic Studies

Uranium

Batch kinetic studies were performed on two soils at the middle initial aqueous phase concentration to determine the approach to equilibrium. The kinetic study results for both soils are presented in Table 5.1 and Figure 5.1 as observed distribution ratio vs. time. Additionally, the difference between an observed distribution ratio and the observed distribution ratio from the previous sampling time is reported as a percentage change in Table 5.1. Sorption behavior for both soils was characterized by an initial rapid increase in observed distribution ratio followed by a slow rate of increase over the remainder of the

Table 5.1 Summary of kinetic study results for uranium on soils 7DS01701KD and I1S-INEEL-109.

| DAYS | 7DS01701KD | | I1S-INEEL-109 | |
	Observed Distribution Ratio[†] mL-g^{-1}	Percent Change %	Observed Distribution Ratio[†] mL-g^{-1}	Percent Change %
7	17.0 ± 1.2	N/A	16.5 ± 0.2	N/A
14	20.8 ± 1.0	22	18.9 ± 0.4	15
28	22.7 ± 1.2	9	19.9 ± 1.0	5
63	23.5 ± 1.0	4	19.2 ± 2.2	-4

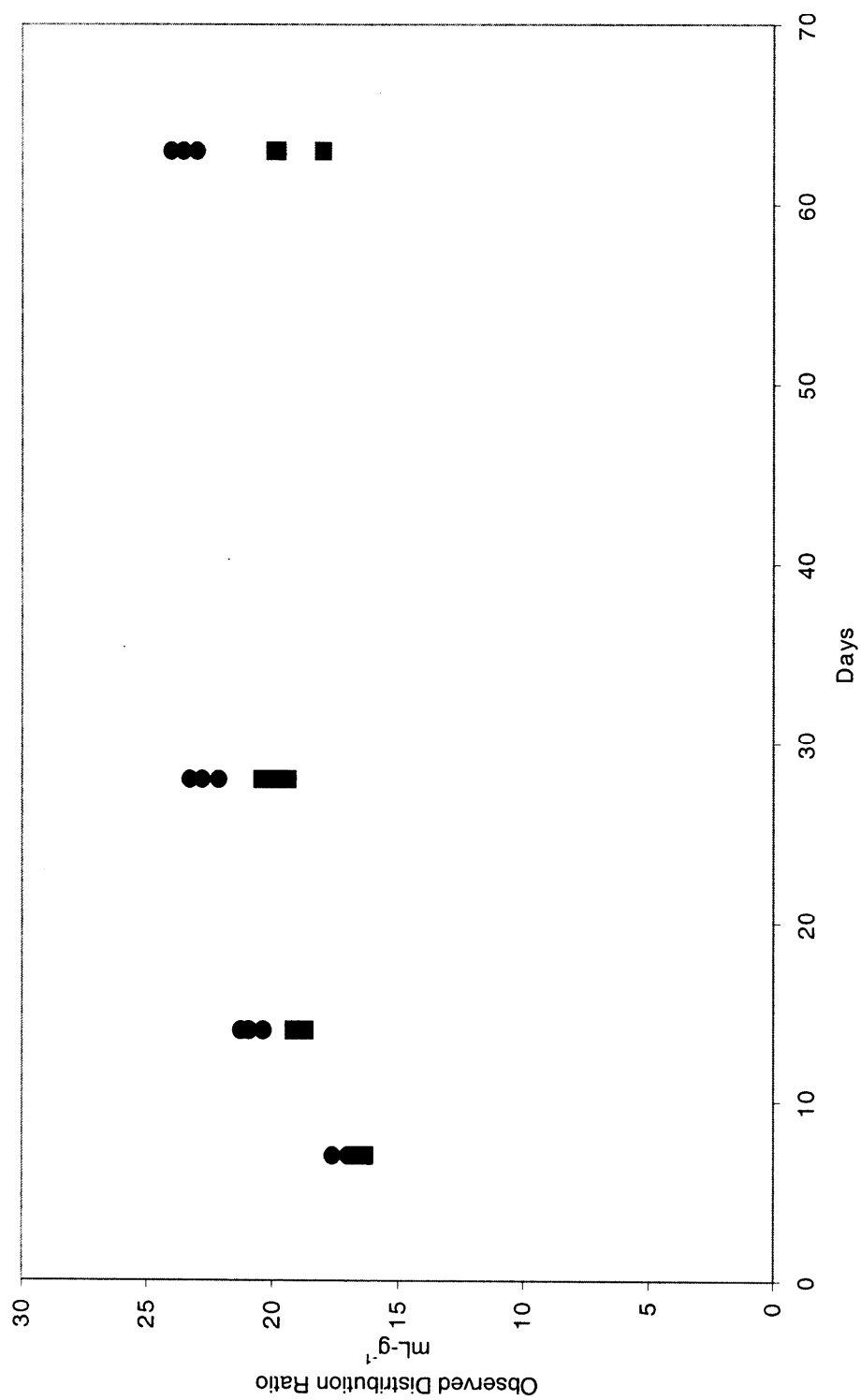[†]Results are reported at ± 95% confidence interval.

Figure 5.1   Results of kinetic study for uranium on two soils: I1S-INEEL-109 (■); 7DS01701KD (●).

study. The observed distribution ratios changed less than 5% for both soils between 28 and 63 days. Although additional uptake of uranium occurred after 28 days, the experimental conditions were considered a sufficient approximation of equilibrium.

Neptunium

The kinetic study results for both soils are presented in Table 5.2 and Figure 5.2. The sorption behavior for both soils was characterized by an initial rapid increase in observed distribution ratio followed by a slow rate of increase over the remainder of the study. Observed distribution ratios still varied by approximately 15% between 28 and 56 days resulting from the continued uptake of neptunium during this period. This uptake indicated that kinetic constraints were likely exerting influence on sorption behavior and equilibrium had not yet been attained. Although additional long-term uptake was likely, 56 days was

Table 5.2   Summary of kinetic study results for neptunium on soils 7DS01701KD and I1S-INEEL-109.

DAYS	7DS01701KD		I1S-INEEL-109	
	Observed Distribution Ratio[†] mL-g^{-1}	Percent Change %	Observed Distribution Ratio[†] mL-g^{-1}	Percent Change %
7	58.5 ± 1.3	N/A	195.4 ± 6.3	N/A
14	68.1 ± 4.7	16	227.0 ± 13.1	16
28	80.8 ± 6.3	19	257.4 ± 16.1	13
56	94.9 ± 2.9	18	285.9 ± 24.1	11

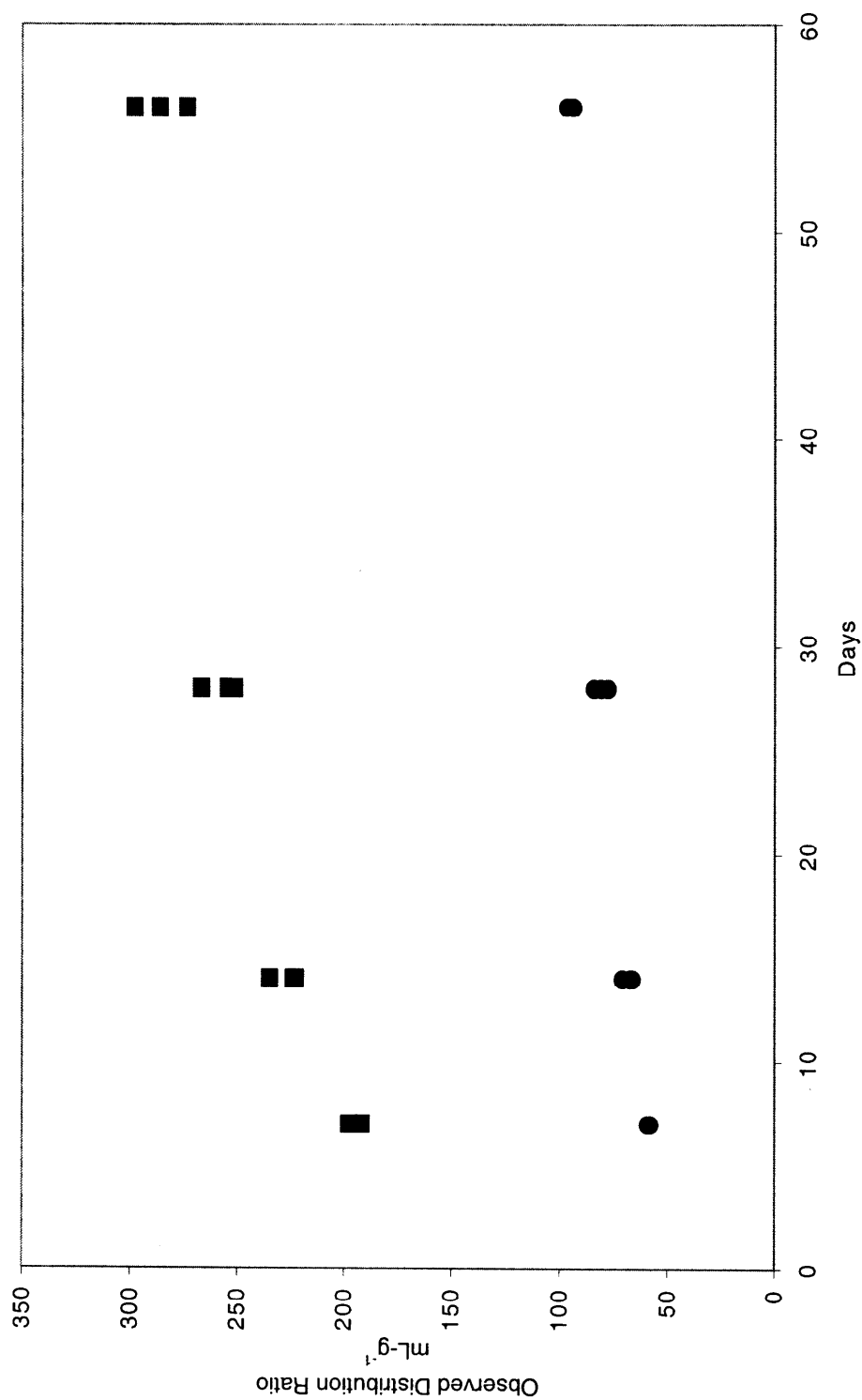[†]Results are reported at ± 95% confidence interval.

Figure 5.2   Results of kinetic study for neptunium on two soils: I1S-INEEL-109 (■); 7DS01701KD (●).

considered sufficient time to approximate equilibrium conditions to complete the batch equilibrium studies in a timely manner.

Americium

Solubility studies were performed with blanks (no soil) to determine an initial aqueous phase concentration that would avoid precipitation of potentially insoluble americium carbonate species during batch kinetic and equilibrium studies. Aliquots of GWS were filtered at nominal 12 nm, spiked with americium, and agitated for short time periods. Aqueous phase concentrations were measured both before and after filtration following agitation. The results from these studies are presented in Table 5.3 as aqueous phase concentrations before and after filtration accompanied by the percentage of aqueous phase concentration lost during filtration.

Table 5.3   Summary of americium losses from short-term blanks (no soil) in GWS.

	AQUEOUS PHASE CONCENTRATION pH: 7.7±0.2		
TIME	Prefiltration	Postfiltration	Percent Loss
days	$Bq\text{-}mL^{-1}$	$Bq\text{-}mL^{-1}$	%
0	37.1	N/A	N/A
1	11.6	8.4	28
0	8.5	7.8	8.2
1	5.7	3.6	37
0	3.3	1.9	42
2	1.9	0.7	63

In the first solubility study, the concentration measured before filtration decreased 69% up to 1 day. Additionally, at 1 day, 28% of the americium was removed by filtration. A second study was conducted with an initial aqueous concentration set near 8.4 $Bq\text{-}mL^{-1}$, which was the remaining dissolved americium from the first study. Again, a loss, 33%, was observed in the unfiltered samples up to 1 day, and at 1 day 37% was lost to filtration. This loss was smaller than the first study probably because of the lower initial concentration. The dissolved americium concentration at 1 day for the second study was 3.6 $Bq\text{-}mL^{-1}$. This value was used as an upper limit for the third study, which was performed at an initial aqueous concentration of 3.3 $Bq\text{-}mL^{-1}$. The loss observed in the unfiltered samples was 42% up to 2 days. The final dissolved americium concentration was 0.7 $Bq\text{-}mL^{-1}$ and the associated loss to filtration was 63 percent at 2 days. This larger loss than in the second study was likely due to the longer time period of the study. The results indicated loss of dissolved americium even at concentrations below 2 $Bq\text{-}mL^{-1}$. The cause of the americium loss was likely preciptiation of $AmOHCO_3(c)$, which has been shown to maintain dissolved americium below 10^{-8} M between pH 7 and 9 in the presence of sufficient carbonate (Silva and Nitsche, 1984; Runde *et al.*, 1992; Vitorge, 1992). Consequently, no batch kinetic or equilibrium studies were performed because a suitable range of aqueous phase concentrations could not be maintained at the low soluble concentrations.

Chromium

Solubility studies were performed with blanks (no soil) to determine an initial aqueous phase concentration that would avoid precipitation of potentially insoluble chromium hydroxide species during batch kinetic and equilibrium studies. Aliquots of GWS were filtered at nominal 12 nm, spiked with chromium, and agitated for short time periods. Two aliquots were withdrawn from the samples to measure aqueous phase concentrations before and after filtration. The results from these studies are presented in Table 5.4 as aqueous phase concentrations before and after filtration accompanied by the percentage of aqueous phase concentration lost during filtration over time.

Initially, the total dissolved chromium concentration was 37.3 Bq-mL^{-1} for the first solubility study. Loss of dissolved chromium was not observed until 1 day at which point 6.2% of the total chromium had precipitated. Between 1 and 3 days, the loss of total chromium was 7.2%. Additionally, 2.9% of the total

Table 5.4   Summary of chromium losses from short-term blanks (no soil) in GWS.

TIME	AQUEOUS PHASE CONCENTRATION pH: 7.6±0.3		
	Prefiltration	Postfiltration	Percent Loss
days	Bq-mL^{-1}	Bq-mL^{-1}	%
0	37.3	37.3	0
1	37.3	35.0	6.2
3	34.6	33.6	2.9
0	32.3	31.8	1.5
1	29.8	29.4	1.3

chromium observed at 3 days had precipitated. The final dissolved concentration was 33.6 Bq-mL^{-1}. This concentration was used as an upper limit for the second solubility study in which the initial concentration was 32.3 Bq-mL^{-1}. The total chromium concentration dropped 7.7% between 0 and 1 day. At 1 day, 1.3% of the total observed chromium was precipitated. The losses of chromium observed in these studies were relatively small so an initial concentration of approximately 35 Bq-mL^{-1} was set as the upper limit for kinetic and batch studies.

Providing a sufficient range of aqueous phase concentrations for the batch studies would have been difficult below 35 Bq-mL^{-1}. Therefore, three solids concentrations, approximately 1,000, 5,000, and 50,000 mg-L^{-1}, were selected to provide a sufficiently broad range to observe sorption isotherms for chromium.

Batch kinetic studies were then performed at the single initial concentration, as determined from short-term solubility studies, and middle solids concentration for both soils to quantify the approach to equilibrium. The results are presented in Table 5.5 and Figure 5.3. The sorption behavior for both soils was characterized by an initial rapid increase in observed distribution ratio followed by a slow rate of decrease over the remainder of the study. Between 28 and 56 days the observed distribution ratios changed less than 15% for both soils. Changes in the observed distribution ratios between 28 and 56 days suggest kinetic limitations were still exerting influence on sorption behavior. However, 56 days was considered a sufficient approximation of equilibrium to complete the batch equilibrium studies in a timely manner.
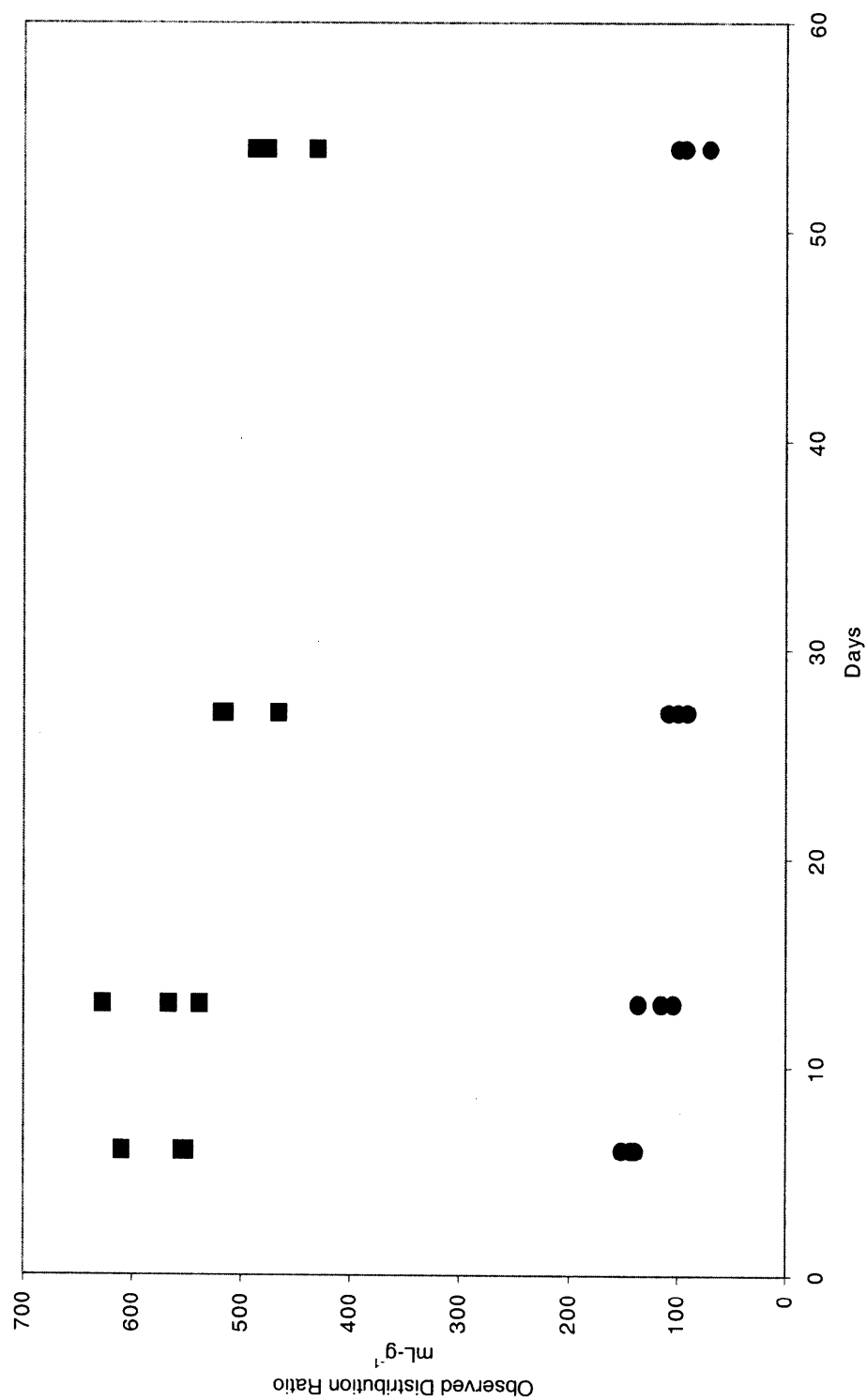
Figure 5.3 Results of kinetic study for chromium on two soils: I4D-INEEL-234 (■); 7DS00901KD (●).

Table 5.5 Summary of kinetic study results for chromium on soils 7DS00901KD and I4D-INEEL-234.

DAYS	7DS00901KD		I4D-INEEL-234	
	Observed Distribution Ratio[†] mL-g^{-1}	Percent Change %	Observed Distribution Ratio[†] mL-g^{-1}	Percent Change %
7	135.8 ± 12.2	N/A	551.6 ± 62.5	N/A
14	110.4 ± 31.4	-19	557.1 ± 86.2	1
28	92.0 ± 16.9	-17	481.9 ± 56.4	-14
56	80.5 ± 29.2	-13	447.9 ± 57.4	-7

[†]Results are reported at ± 95% confidence interval.

The decay of radioactive chromium-51 ($t_{1/2}$ = 27.8 d) was a potentially significant process occurring during the kinetic studies. Concentrations of its decay product, vanadium, reached approximately 75% of the initial aqueous phase chromium concentration over the duration of the studies. The increasing competition between chromium and vanadium as the latter became more concentrated is a likely explanation for the slow decrease in observed distribution ratios. Khan *et al.* (1995) observed a similar phenomenon for radioactive trivalent chromium-51 sorption onto bentonite at pH 3.5.

Batch Equilibrium Studies

Uranium

The partitioning data for uranium were collected between 48 and 56 days, and are presented in Appendix B as sorbed phase concentration vs. aqueous phase concentration. The resulting sorption isotherms are presented in Figure 5.4 for typical soil sample 7DS01701KD and in Appendix C for all other soil
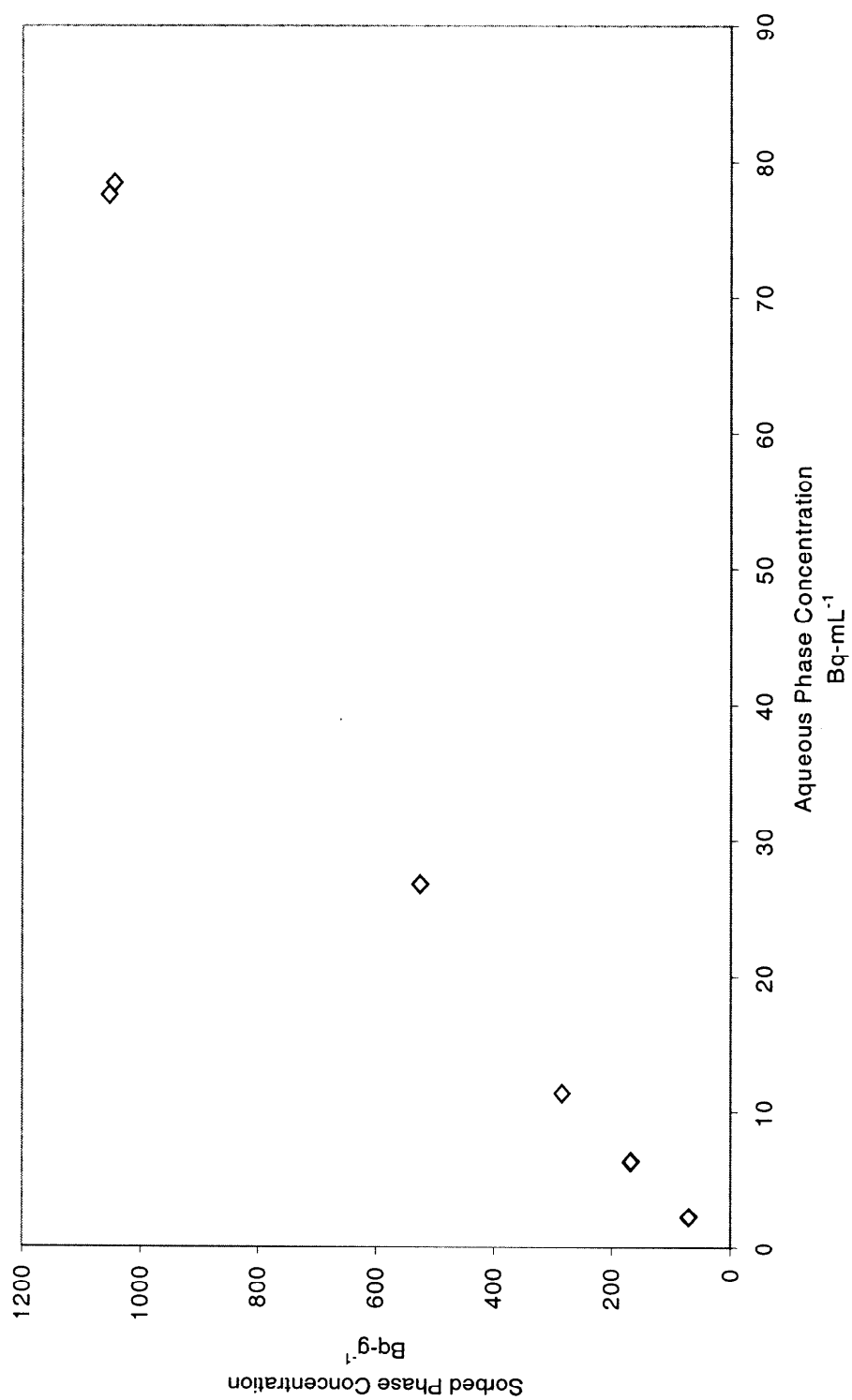
Figure 5.4   Results of equilibrium study for uranium on soil: 7DS01701KD ($\Diamond$).

samples. The isotherms for all soils were characterized by a decreasing rate of increase in sorbed phase concentration with increasing aqueous phase concentration. This characterization is representative of nonlinear sorption behavior.

The observed non-linearity of the sorption data may reflect uranium sorption to distinct surface sites as a function of surface loading. Morris *et al.* (1994) and Chisholm-Brause *et al.* (1994) detected uranium sorption to distinct sites on pure montmorillonite surfaces as uranium concentration increased. In heterogeneous soils, as in this study, a greater potential may exist for a variety of surface binding sites with differing affinities for uranium species leading to the observed nonlinear sorption behavior.

Two empirical nonlinear sorption isotherm models, Langmuir and Freundlich, were fit to the partitioning data. The model fits are presented in Figure 5.5 for typical soil sample 7DS01701KD and Appendix C for all other soil samples. Table 5.6 presents a summary of sorption model parameters and their respective statistics of model fit. Based on the regression coefficients, the Freundlich model ($0.99 \leq R^2 \leq 1.00$) characterized the data better than the Langmuir model ($0.61 \leq R^2 \leq 0.98$). The Langmuir model is based on a constant energy of association for sorption sites, whereas the Freundlich model is based on a distribution of energies of association. Because the Freundlich model fit the data better than the Langmuir model, the possibility for multiple sorption sites with distinct affinities may exist for uranium on the INEEL soils.
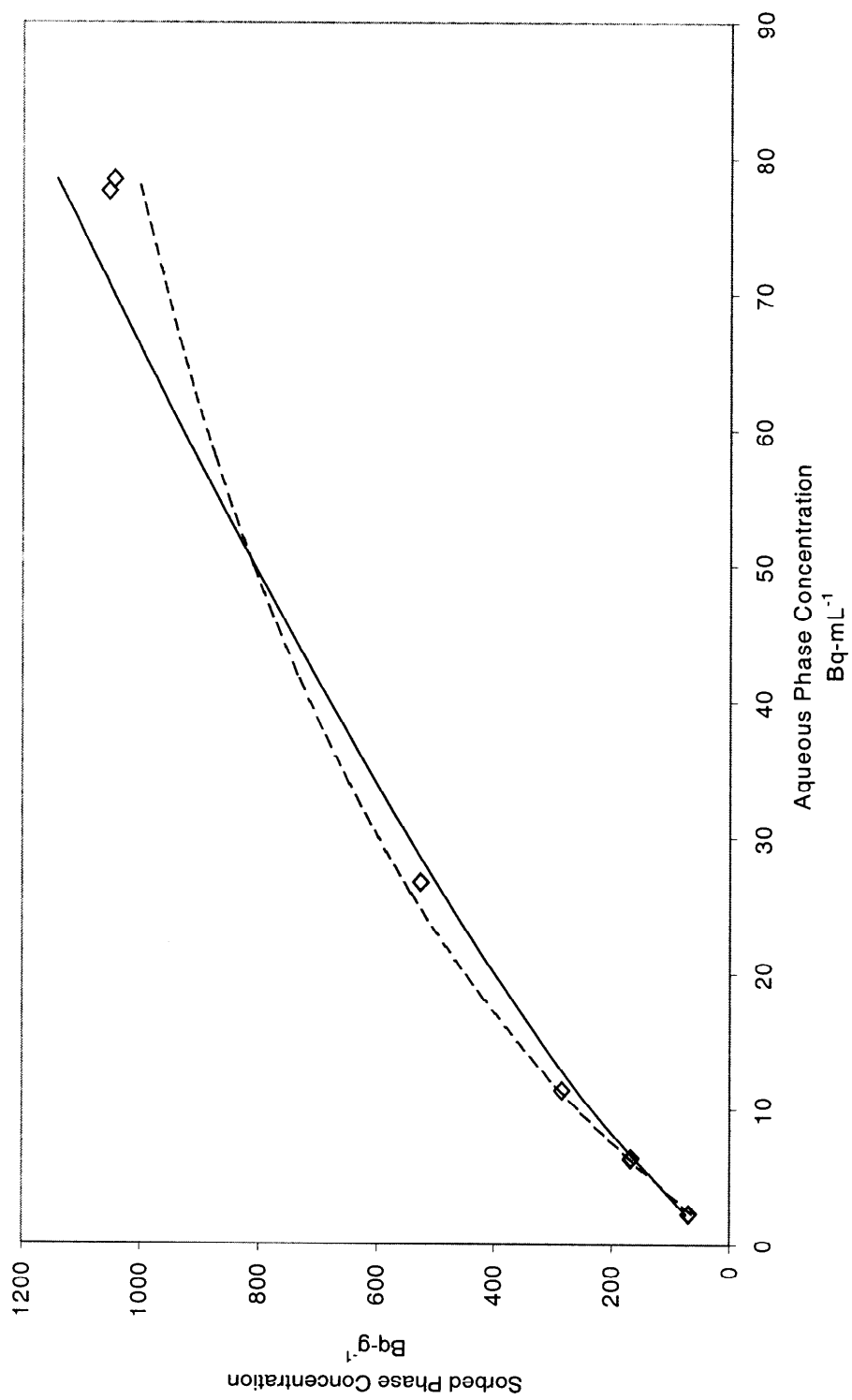
Figure 5.5   Application of sorption models to results of equilibrium study for uranium on soil 7DS01701KD ($\Diamond$).
Solid line represents the fitted Freundlich model. Dashed line represents the fitted Langmuir model.

Table 5.6   Summary of sorption models with respective statistics of model fit determined from the results of the equilibrium study for uranium on all soils.

SOIL	LANGMUIR			FREUNDLICH		
	$K_L^{\dagger}$ $mL\text{-}Bq^{-1}$	$S_{max}^{\dagger}$ $Bq\text{-}g^{-1}$	R^2	$K_F^{\dagger}$ $mL^n\text{-}g^{-n}$	$n^{\dagger}$	R^2
7DS00101KD	0.025 ± 0.006	2628 ± 482	0.90	74 ± 0.8	0.81 ± 0.027	1.00
7DS00301KD	0.020 ± 0.002	2165 ± 241	0.96	54 ± 1.8	0.78 ± 0.045	0.99
7DS00501KD	0.015 ± 0.006	2014 ± 841	0.61	38 ± 2.6	0.79 ± 0.061	0.99
7DS00701KD	0.012 ± 0.004	1891 ± 490	0.80	33 ± 1.2	0.77 ± 0.061	0.99
7DS00901KD	0.021 ± 0.004	1715 ± 384	0.85	47 ± 1.2	0.75 ± 0.045	0.99
7DS01701KD	0.018 ± 0.002	1736 ± 214	0.95	40 ± 1.0	0.77 ± 0.039	0.99
7DS02301KD	0.013 ± 0.008	2099 ± 290	0.94	35 ± 1.8	0.81 ± 0.039	1.00
I2S-INEEL-105	0.017 ± 0.004	1796 ± 288	0.92	40 ± 1.0	0.78 ± 0.037	1.00
I1S-INEEL-109	0.014 ± 0.002	1880 ± 308	0.92	35 ± 1.4	0.78 ± 0.043	0.99
I4D-INEEL-224	0.011 ± 0.002	2157 ± 461	0.87	31 ± 1.2	0.81 ± 0.033	1.00
I3D-INEEL-229	0.012 ± 0.002	1595 ± 114	0.98	28 ± 1.2	0.77 ± 0.047	0.99
I4D-INNEL-231	0.016 ± 0.002	1471 ± 196	0.94	32 ± 1.2	0.76 ± 0.041	0.99
I1D-INNEL-234	0.008 ± 0.002	4194 ± 582	0.95	40 ± 1.0	0.87 ± 0.033	1.00
I4D-INNEL-234	0.010 ± 0.002	1418 ± 159	0.96	23 ± 1.0	0.76 ± 0.043	0.99

†Results are reported at ± 95% confidence interval.

Barnett *et al.* (2000) also employed the Freundlich model to characterize uranium sorption data onto subsurface media from the Oak Ridge National Laboratory (ORNL) in Tennessee, the Savannah River Site (SRS) in South Carolina, and the Hanford Reservation (HR) in Washington. The Freundlich parameters determined by Barnett *et al.* (2000) are presented with the results of this study in Table 5.7. Their departure from linearity was larger than in this study. Additionally, the sorption capacity, K_F, of their soils was found to be approximately an order of magnitude larger than those examined in this study.

The Freundlich sorption capacity ($23\pm1.0 \leq K_F \leq 74\pm0.8$) varied by approximately a factor of three among all the soil samples. This variability is relatively small given the highly heterogeneous nature of subsurface environments such as those at the INEEL. Therefore the sorption capacity of the INEEL soils for uranium may be fairly uniform with depth.

Table 5.7   Comparison of uranium Freundlich isotherm parameters for soils from Oak Ridge National Laboratory (ORNL), Savannah River Site (SRS), Hanford Reservation (HR), and the Idaho National Engineering and Environmental Laboratory (INEEL).

SOIL	FREUNDLICH PARAMETERS		
	$K_F^{\dagger}$ $mL^n\text{-}g^{-n}$	$n^{\dagger}$	R^2
ORNL[¶]	450 ± 30	0.67 ± 0.04	0.99
SRS[¶]	230 ± 7	0.68 ± 0.02	1.00
HR[¶]	480 ± 10	0.56 ± 0.03	0.99
INEEL	39 ± 25	0.78 ± 0.06	0.99

[†]Results are reported at $\pm$ 95% confidence interval.
[¶]Adapted from Barnett *et al.* (2000).

Neptunium

The partitioning data for neptunium were collected at 56 days. They are presented in Appendix B as sorbed phase concentration vs. aqueous phase concentration. The resulting sorption isotherms are presented Figure 5.6 for typical soil sample 7DS01701KD and in Appendix D. As observed for uranium, the sorption behavior for all soils was characterized by a decreasing rate of increase in sorbed phase concentrations with increasing aqueous phase concentrations, which is representative of nonlinear sorption behavior.

The observed non-linearity of the sorption data may reflect neptunium sorption to distinct surface sites as a function of surface loading. Kozai *et al.* (1993), Nagasaki *et al.* (1998), and Nagasaki and Tanaka (2000) postulated two distinct sorption behaviors for neptunium on pure clay minerals: a fast ion exchange process onto outer surface sites and a slower specific sorption onto interlayer surfaces. In heterogeneous soils, as in this study, a greater potential may exist for a variety of surface binding sites.

Two empirical nonlinear sorption isotherm models, Langmuir and Freundlich, were fit to the partitioning data. The model fits are presented in Figure 5.7 for typical soil sample 7DS01701KD and Appendix D for all other soil samples. A summary of sorption model parameters and their respective statistics of model fit are presented in Table 5.8. As observed for uranium, the Freundlich model ($0.98 \leq R^2 \leq 1.00$) characterized the neptunium data better than the Langmuir model ($0.62 \leq R^2 \leq 0.80$). The improved agreement of the Freundlich model over the Langmuir model may suggest that multiple sorption sites with distinct affinities exist for neptunium on the INEEL soils.
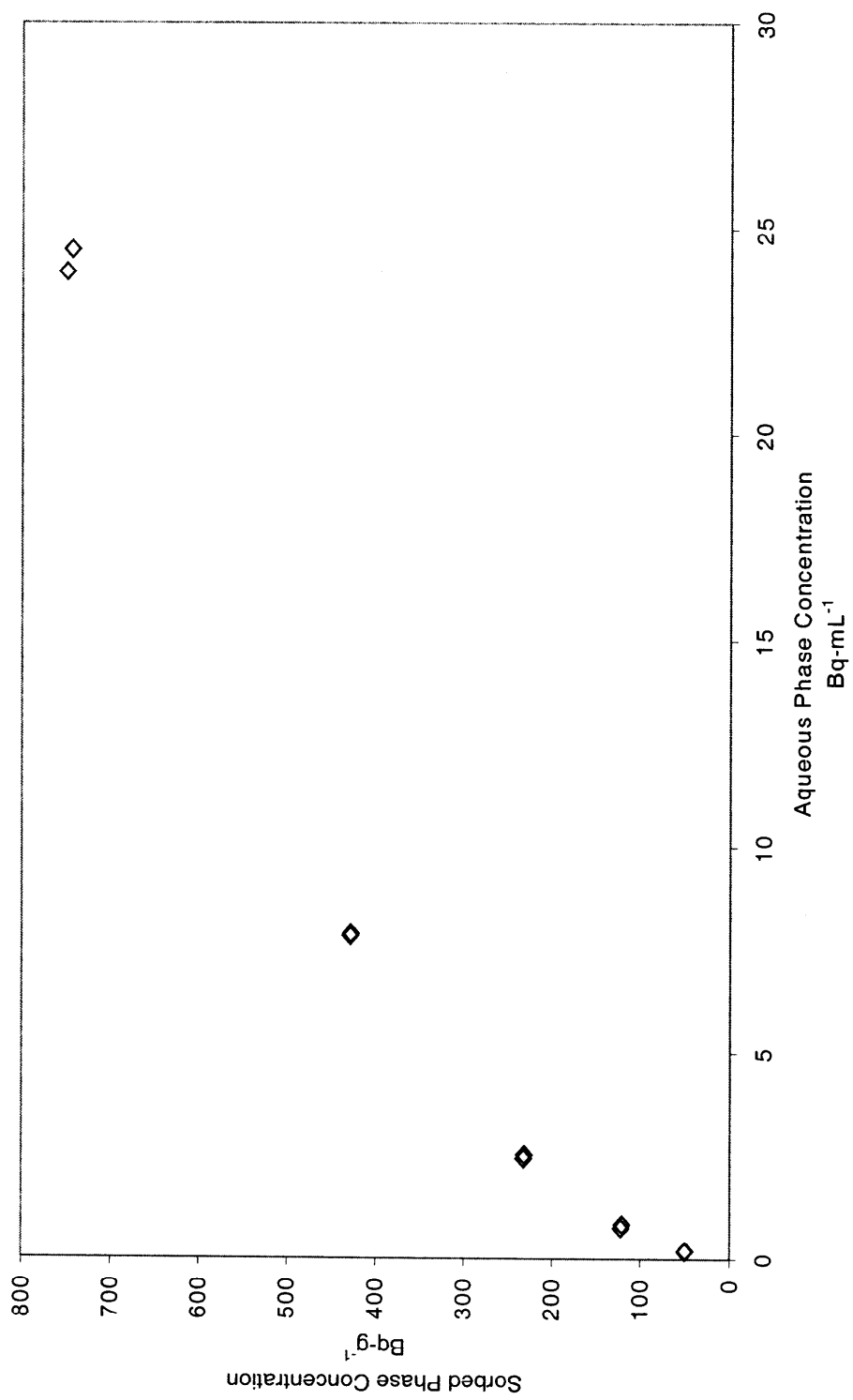
Figure 5.6   Results of equilibrium study for neptunium on soil: 7DS01701KD (◊).
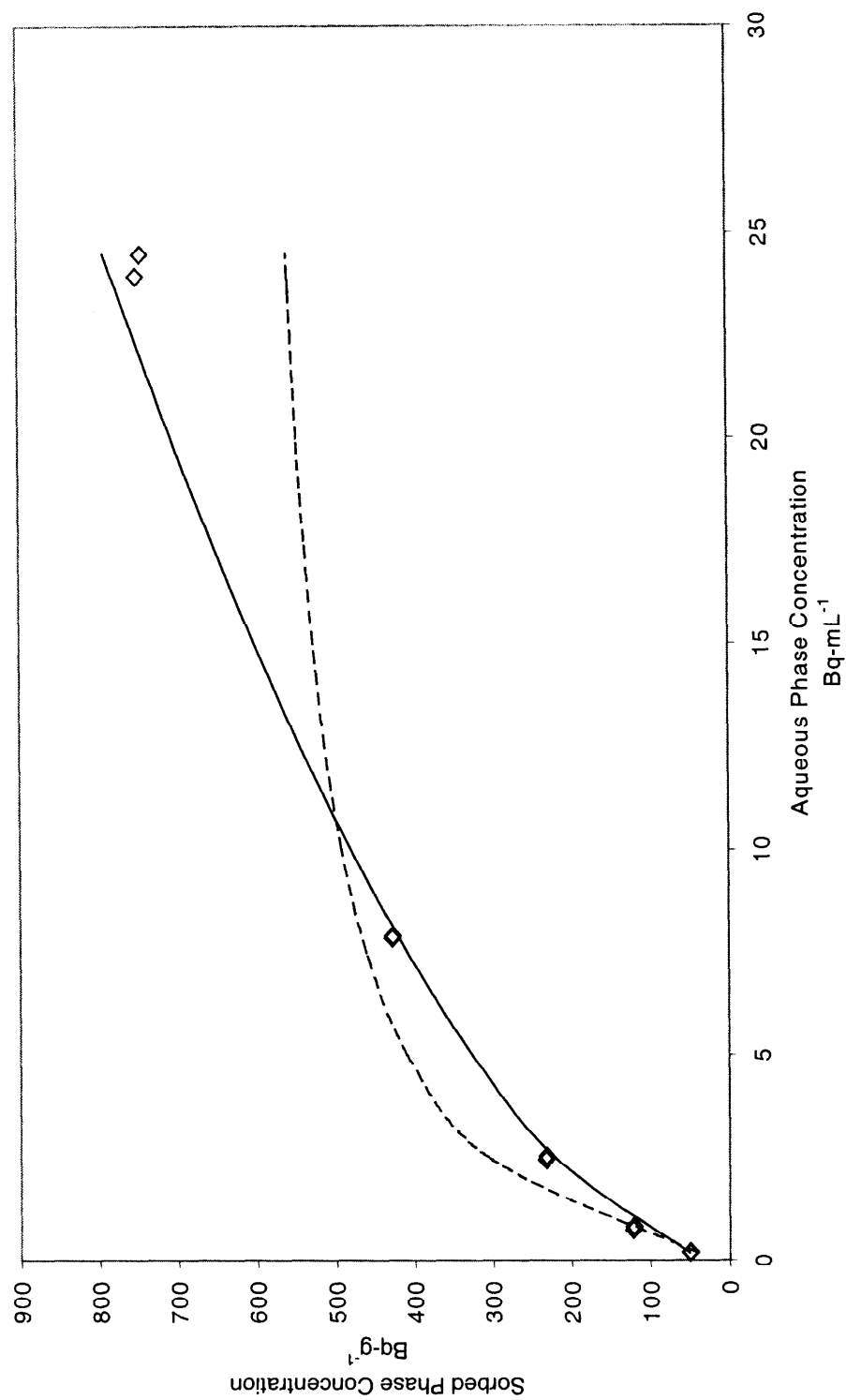
Figure 5.7   Application of sorption models to results of equilibrium study for neptunium on soil 7DS01701KD (◇). Solid line represents the fitted Freundlich model. Dashed line represents the fitted Langmuir model.

Table 5.8   Summary of sorption models with respective statistics of model fit determined from the results of the equilibrium study for neptunium on all soils.

SOIL	LANGMUIR			FREUNDLICH		
	$K_L{}^\dagger$ mL-Bq^{-1}	$S_{max}{}^\dagger$ Bq-g^{-1}	R^2	$K_F{}^\dagger$ mL^n-g^{-n}	$n^\dagger$	R^2
7DS00101KD	0.89 ± 0.45	720 ± 220	0.66	246 ± 2.0	0.59 ± 0.022	1.00
7DS00301KD	0.20 ± 0.10	619 ± 188	0.65	91 ± 1.0	0.62 ± 0.012	1.00
7DS00501KD	0.31 ± 0.11	814 ± 196	0.75	155 ± 3.9	0.56 ± 0.027	1.00
7DS00701KD	0.05 ± 0.02	625 ± 143	0.79	38 ± 0.4	0.65 ± 0.035	0.99
7DS00901KD	0.19 ± 0.10	633 ± 147	0.77	92 ± 0.4	0.59 ± 0.024	1.00
7DS01701KD	0.40 ± 0.17	617 ± 163	0.71	133 ± 1.2	0.56 ± 0.022	1.00
7DS02301KD	0.35 ± 0.14	550 ± 167	0.62	109 ± 1.0	0.56 ± 0.008	1.00
I2S-INEEL-105	0.08 ± 0.04	616 ± 141	0.80	52 ± 0.4	0.65 ± 0.016	1.00
I1S-INEEL-109	0.65 ± 0.28	977 ± 259	0.73	280 ± 2.2	0.58 ± 0.032	0.99
I4D-INEEL-224	0.53 ± 0.25	653 ± 186	0.67	162 ± 1.6	0.54 ± 0.018	1.00
I3D-INEEL-229	0.79 ± 0.37	809 ± 190	0.78	256 ± 4.1	0.57 ± 0.041	0.99
I4D-INNEL-231	0.42 ± 0.22	559 ± 153	0.68	124 ± 1.2	0.53 ± 0.016	1.00
I1D-INNEL-234	0.18 ± 0.09	696 ± 212	0.64	95 ± 1.0	0.60 ± 0.020	1.00
I4D-INNEL-234	0.18 ± 0.08	583 ± 149	0.69	76 ± 2.4	0.60 ± 0.024	0.98

†Results are reported at ± 95% confidence interval.

Nagasaki *et al.* (1998) and Nagasaki and Tanaka (2000) also observed nonlinear sorption behavior of neptunium onto pure Na-montmorillonite and illite. The researchers reported a satisfactory description of the data with the Freundlich sorption model. However, they observed a spectrum of sorption affinities onto these clays, which reportedly afforded a better understanding of the degree of heterogeneity of the surfaces than the simple Freundlich model, and a direct comparison of Freundlich parameters is not possible.

The Freundlich sorption capacity ($38\pm0.4 \leq K_F \leq 280\pm2.2$) varied by a factor of approximately eight among all the soil samples. Although the variability was greater than was observed for uranium, it is still not large considering typical subsurface heterogeneity. Therefore the sorption capacity of the INEEL soils for neptunium may be fairly uniform with depth.

Chromium

Batch equilibrium studies for chromium were performed at the single initial aqueous phase concentration and a range of solids concentrations to provide a sufficient range of equilibrium aqueous phase concentrations. The partitioning data are presented in Table 5.9 for all soil samples as initial aqueous phase concentration decay corrected to the sampling time, 56 days, and the aqueous phase concentration measured at the sampling time. The loss of aqueous phase chromium was typically less in samples with a solids concentration that approximated 50,000 mg-L^{-1} than in samples with a solids concentration that approximated 1,000 mg-L^{-1}. This observation was not expected since a larger number of sorption sites would be expected with a higher solids concentration,

Table 5.9 Summary of equilibrium study data for chromium on fourteen soil samples and blanks.

Solids mg-L^{-1}	CONCENTRATIONS Initial Aqueous Phase Decay Corrected To 56 Days[†] Bq-mL^{-1}	Aqueous Phase[†] Bq-mL^{-1}
pH: 7.9±0.1		
7DS00101KD		
954 ± 41	6.9 ± 0.2	1.7 ± 0.0
4868 ± 262	6.9 ± 0.2	2.2 ± 0.1
51000 ± 655	6.9 ± 0.2	1.8 ± 0.6
7DS00301KD		
928 ± 58	6.9 ± 0.2	3.0 ± 0.7
4830 ± 36	6.9 ± 0.2	3.8 ± 0.2
49882 ± 592	6.9 ± 0.2	4.1 ± 0.8
7DS00501KD		
752 ± 121	6.9 ± 0.2	2.5 ± 0.4
4598 ± 462	6.9 ± 0.2	5.1 ± 1.4
52784 ± 4115	6.9 ± 0.2	6.6 ± 0.6
7DS00701KD		
858 ± 90	6.9 ± 0.2	2.9 ± 0.2
5106 ± 678	6.9 ± 0.2	4.6 ± 1.2
49306 ± 3808	6.9 ± 0.2	4.5 ± 0.2
7DS00901KD		
1062 ± 638	6.9 ± 0.2	2.8 ± 0.0
4650 ± 865	6.9 ± 0.2	4.8 ± 0.0
45156 ± 4716	6.9 ± 0.2	6.0 ± 0.0
7DS01701KD		
854 ± 30	6.9 ± 0.2	1.0 ± 0.6
5238 ± 145	6.9 ± 0.2	1.8 ± 0.0
53324 ± 2110	6.9 ± 0.2	1.9 ± 0.2
7DS02301KD		
968 ± 38	6.9 ± 0.2	2.5 ± 0.4
5086 ± 65	6.9 ± 0.2	3.9 ± 0.4
52758 ± 598	6.9 ± 0.2	4.7 ± 1.4

[†]Results are reported at ± 95% confidence interval.

Table 5.9 continued.

Solids mg-L^{-1}	CONCENTRATIONS Initial Aqueous Phase Decay Corrected To 56 Days† Bq-mL^{-1}	Aqueous Phase† Bq-mL^{-1}
	I2S-INEEL-105	
1028 ± 32	6.9 ± 0.2	1.5 ± 0.4
5334 ± 96	6.9 ± 0.2	2.7 ± 0.3
52762 ± 845	6.9 ± 0.2	3.2 ± 0.4
	I1S-INEEL-109	
738 ± 77	6.9 ± 0.2	1.2 ± 0.1
4046 ± 166	6.9 ± 0.2	0.8 ± 0.1
40212 ± 798	6.9 ± 0.2	0.5 ± 0.4
	I4D-INEEL-224	
632 ± 39	6.9 ± 0.2	0.6 ± 0.1
4764 ± 460	6.9 ± 0.2	2.0 ± 0.1
44766 ± 120	6.9 ± 0.2	3.7 ± 0.0
	I3D-INEEL-229	
772 ± 58	6.9 ± 0.2	0.6 ± 0.1
5072 ± 494	6.9 ± 0.2	1.0 ± 0.6
50644 ± 5186	6.9 ± 0.2	1.7 ± 0.4
	I4D-INEEL-231	
941 ± 62	6.9 ± 0.2	1.7 ± 0.0
4888 ± 225	6.9 ± 0.2	2.5 ± 0.3
51100 ± 1486	6.9 ± 0.2	3.2 ± 0.6
	I1D-INEEL-234	
580 ± 89	6.9 ± 0.2	2.8 ± 1.2
4084 ± 725	6.9 ± 0.2	5.6 ± 0.1
44992 ± 5841	6.9 ± 0.2	6.8 ± 0.3
	I4D-INEEL-234	
564 ± 65	6.9 ± 0.2	1.3 ± 0.1
3918 ± 357	6.9 ± 0.2	2.3 ± 0.3
36008 ± 2313	6.9 ± 0.2	2.3 ± 0.3
	BLANKS	
N/A	6.9 ± 0.2	4.1 ± 0.8

†Results are reported at ± 95% confidence interval.

resulting in more sorption and a subsequent increase in the loss of aqueous phase chromium at the higher solids concentration. Additionally, the loss of chromium from the blanks (no soil) was 41%. Therefore, the precipitation of chromium likely had some influence during the equilibrium studies.

Samples with the highest solids concentration would have had the largest number of sorption sites available, whereas, samples with the lower solids concentrations would have had fewer sites to sorb chromium. Therefore, samples with the highest solids concentration should have less influence from precipitation and be the best indicator of chromium's affinity for the soil. Consequently, apparent distribution ratios were only calculated for samples at the highest solids concentration in an attempt to determine an approximation of chromium's sorption affinity. The results are presented in Table 5.10 for each soil. The apparent distribution coefficients are all relatively small except for soil I1S-INEEL-109. However, given the large variability observed for that soil, its accuracy is questionable. Because the apparent distribution coefficients are all considered low at the highest solids concentration examined, chromium's affinity for the soil is expected to be relatively small.

Table 5.10 Summary of apparent distribution ratios from samples with solids concentrations that approximated 50,000 mg-L^{-1} for all soils.

Soil	Apparent Distribution Ratio[†] mL-g^{-1}		
7DS00101KD	55	±	21
7DS00301KD	14	±	6.50
7DS00501KD	0.8	±	1.90
7DS00701KD	11	±	2.20
7DS00901KD	3.3	±	0.26
7DS01701KD	9.0	±	8.3
7DS02301KD	48	±	9.5
I2S-INEEL-105	22	±	5.8
I1S-INEEL-109	392	±	319
I4D-INEEL-224	19	±	0.6
I3D-INEEL-229	62	±	18
I4D-INEEL-231	23	±	6.8
I1D-INEEL-234	0.11	±	0.72
I4D-INEEL-234	56	±	11

[†]Results are reported at ± 95% confidence interval.

Soil Property Correlations

Analyses were performed to determine if sorption behavior was correlated with common gross soil characteristics. A linear sorption model was fit to the sorption data at the three lowest aqueous phase concentrations to determine an approximation of linear distribution coefficients at the observed maximum sorption affinity. Tables 5.11 and 5.12 list the fitted distribution coefficients and statistics of model fit for uranium and neptunium, respectively, on each soil for which characterization data were available. Soil characterization data are presented in Tables 4.2, 4.3, and 4.4. Specifically, correlations were tested between the distribution coefficients and surface area, cation exchange capacity, clay content, and extractable metal content. The correlation coefficients are

Table 5.11 Summary of linear sorption model with respective statistics of model fit determined from the results of the equilibrium study for uranium at the three lowest aqueous phase concentrations on soils for which characterization data were available.

SOIL	LINEAR MODEL		R^2
	$K^†$ mL-g^{-1}		
7DS00101KD	58	± 1.8	0.99
7DS00301KD	37	± 1.8	0.99
7DS00501KD	24	± 1.2	0.98
7DS00701KD	19	± 1.2	0.98
7DS00901KD	29	± 1.4	0.98
7DS01701KD	26	± 1.0	0.99
7DS02301KD	25	± 0.8	0.99

†Results are reported at ± 95% confidence interval.

Table 5.12 Summary of linear sorption model with respective statistics of model fit determined from the results of the equilibrium study for neptunium at the three lowest aqueous phase concentrations on soils for which characterization data were available.

SOIL	LINEAR MODEL		R^2
	$K^†$ mL-g^{-1}		
7DS00101KD	295	± 37	0.92
7DS00301KD	55	± 8.8	0.86
7DS00501KD	111	± 20	0.82
7DS00701KD	17	± 2.2	0.89
7DS00901KD	59	± 9.2	0.86
7DS01701KD	100	± 18	0.82
7DS02301KD	68	± 13	0.82

†Results are reported at ± 95% confidence interval.

listed in Table 5.13 for both uranium and neptunium. Correlations were not tested for chromium due to the inability to determine distribution coefficients from the equilibrium data. The correlation coefficients ranged from 0.07 to 0.88 and 0.15 to 0.90 for uranium and neptunium, respectively.

Table 5.13 Summary of statistical correlations between the fitted linear sorption model and available soil properties.

SOIL PROPERTY	CORRELATION COEFFICIENT	
	Uranium	Neptunium
Surface Area	0.82	0.54
CEC	0.88	0.81
Clay Content	0.07	0.15
SiO_2	0.62	0.90
Al_2O_3	0.47	0.21
Fe_2O_3	0.44	0.42
MnO	0.88	0.48

Some of the correlation coefficients appear to suggest a fairly strong correlation for both uranium and neptunium. However, the actual range of soil properties is relatively small, and the correlation coefficients reported may actually be scatter about the small range of a possible relation. For instance, correlations with cation exchange capacity resulted in fairly strong correlation coefficients, 0.88 and 0.81 for uranium and neptunium, respectively. However, the soil property itself only varied from 14.8 to 43.9 meq-100g^{-1} among the seven characterized soils. This variation appears relatively small given that in highly heterogeneous subsurface environments large variations in soil properties are possible.

Ligand Studies

Batch ligand studies were performed to examine the effect of bicarbonate, sulfate, and fluoride on sorption behavior. The studies were performed on two soils over a range of three initial radionuclide aqueous phase concentrations for uranium and neptunium. Ligand studies were not performed with chromium because of the dominance of hydroxides on chromium aqueous speciation.

Inorganic carbon concentrations measured in background (no activity) samples are presented in Table 5.14 for the two soil samples in each groundwater simulant. As expected, GWS had the highest inorganic carbon concentration, while GWS(-CO_3^{2-}) and GWS(-CO_3^{2-}, SO_4^{2-}, F⁻) were characterized with smaller amounts of inorganic carbon.

The experimentally measured concentration of inorganic carbon in GWS was lower than the concentration at which GWS was originally prepared due to the formation of insoluble carbonate species such as calcite. To minimize the effect of the precipitated species on sorption behavior, the simulant was allowed to become quiescent to settle out precipitates. GWS was then decanted from the top of the simulant reservoir for use in these studies. Inorganic carbon was likely introduced to GWS(-CO_3^{2-}) and GWS(-CO_3^{2-}, SO_4^{2-}, F⁻) samples largely from the dissolution of carbonate from the soil samples during the incubation period. Contributions from atmospheric carbon dioxide added approximately 0.15 mg-L^{-1}.

Table 5.14 Summary of inorganic carbon concentrations determined in background (no activity) samples at equilibrium for soils I2S-INEEL-105 and I4D-INEEL-234.

SIMULANT	I2S-INEEL-105 Inorganic Carbon mg-L^{-1}	I4D-INEEL-234 Inorganic Carbon mg-L^{-1}
GWS	22 ± 0.20	27 ± 1.2
GWS(-CO_3^{2-})	3.8 ± 0.80	9.6 ± 1.2
GWS(-CO_3^{2-}, SO_4^{2-}, F⁻)	3.9 ± 0.22	9.6 ± 0.92

†Results are reported at ± 95% confidence interval.

Uranium

The partitioning data for uranium are presented in Appendix B as sorbed phase concentration vs. aqueous phase concentration for both soils. Sorption isotherms are presented in Figures 5.8 and 5.9 for soil samples I2S-INEEL-105 and I4D-INEEL-234, respectively. The sorption behavior of soil I2S-INEEL-105 was characterized by a sharp increase in sorbed phase concentration over the entire aqueous phase concentration range for both GWS($-CO_3^{2-}$) and GWS($-CO_3^{2-}$, SO_4^{2-}, F^-). Additionally, loss of uranium in blanks (no soil) averaged 59±21% and 43±19% for GWS($-CO_3^{2-}$) and GWS($-CO_3^{2-}$, SO_4^{2-}, F^-), respectively. The combination of the sharp increase in the sorption isotherm for uranium and the large the loss of uranium in the blanks (no soil) suggests that the observed increase in sorbed phase concentration was likely influenced by the precipitation of uranium in the absence of sufficient inorganic carbon, which is known to increase uranium solubility.

Sorption behavior for soil sample I4D-INEEL-234 in GWS($-CO_3^{2-}$) and GWS($-CO_3^{2-}$, SO_4^{2-}, F^-) was characterized by increasing sorbed phase concentration with increasing aqueous phase concentration. The rate of increase in sorbed phase concentration decreased with increasing aqueous phase concentration. This behavior, which was also observed with the GWS, is typical of nonlinear sorption. However, somewhat larger sorbed phase concentrations were observed for a given aqueous phase concentration in GWS($-CO_3^{2-}$) and GWS($-CO_3^{2-}$, SO_4^{2-}, F^-) vs. GWS. The sorbed phase concentrations probably did not reflect true uptake by the soil and were somewhat inflated by the loss of aqueous phase activity to precipitation.
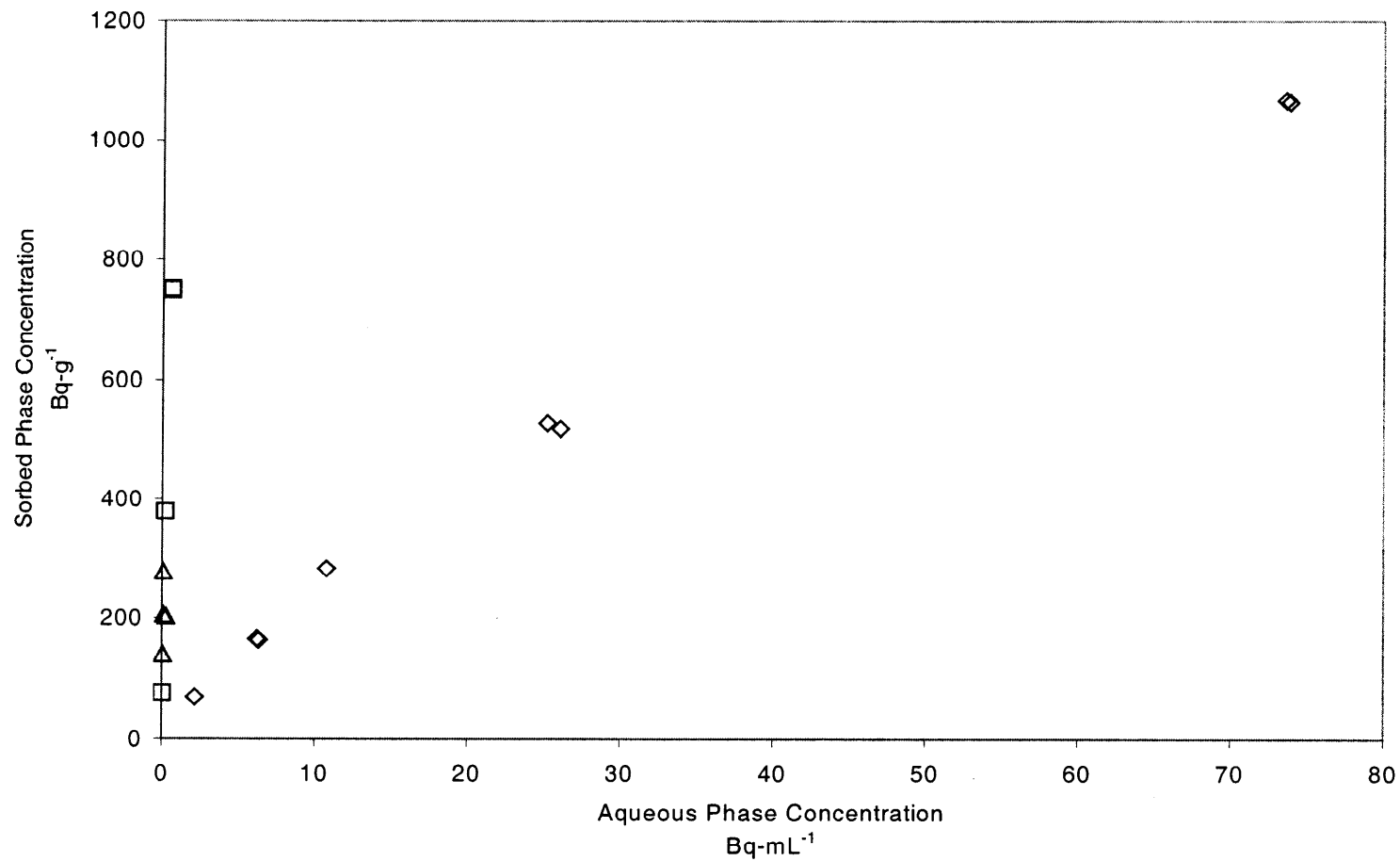
Figure 5.8   Results of ligand study for uranium on soil I2S-INEEL-105 for GWS (◊); GWS (-CO$_3^{2-}$) (□); GWS (-CO3^{2-}, SO$_4^{2-}$, F$^-$) (△).
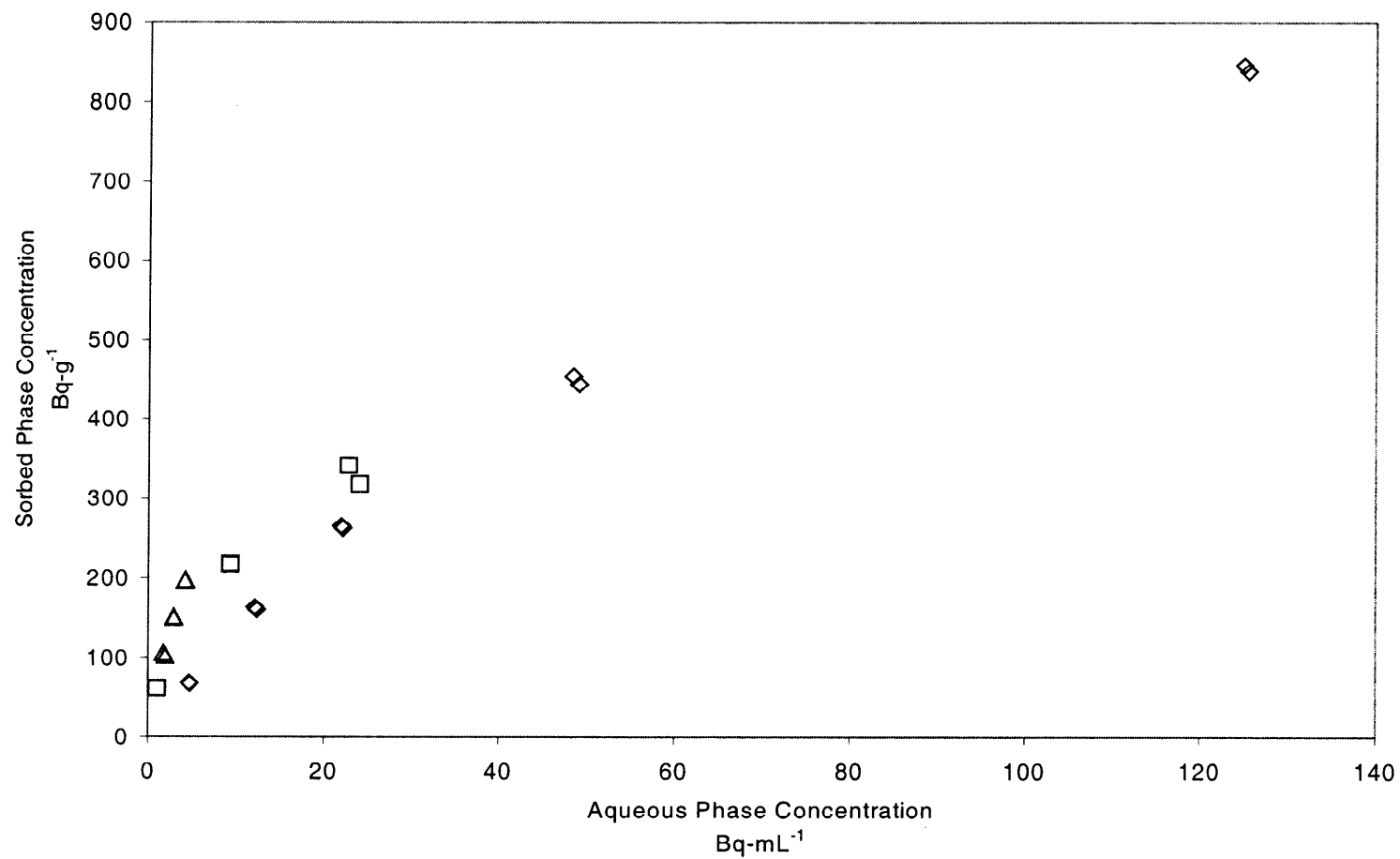
Figure 5.9   Results of ligand study for uranium on soil I4D-INEEL-234 for GWS (◊); GWS (-CO$_3^{2-}$) (□);GWS (-CO3^{2-}, SO$_4^{2-}$, F$^-$) (Δ).

The loss of uranium in blanks (no soil) averaged 59±21% and 43±19% for GWS(-CO_3^{2-}) and GWS(-CO_3^{2-}, SO_4^{2-}, F‾), respectively. However, the amount lost from the partitioning samples was likely less than the observed losses from the blanks (no soil) because the concentration of inorganic carbon was expected to be larger in the partitioning samples than the blanks due to carbonate dissolution from the soil. More inorganic carbon would have resulted in the increased formation of carbonate species, which would have increased the amount of soluble uranium. Because of the effect of carbonate on uranium behavior, and the inability to determine the exact influence of precipitation on the sorption isotherms, the effect of sulfate and fluoride was not clear from the experimental results.

Neptunium

The partitioning data for neptunium are presented in Appendix B as sorbed phase concentration vs. aqueous phase concentration. Sorption isotherms are presented in Figures 5.10 and 5.11 for soil samples I2S-INEEL-105 and I4D-INEEL-234, respectively. The isotherm for each simulant was characterized by a nonlinear sorption pattern. Additionally, both soils were characterized by similar sorption behavior for all three groundwater simulants.

The Freundlich sorption model was fit to the partitioning data. Table 5.15 presents a summary of sorption model parameters and their respective statistics of model fit. Based on the regression coefficients, the Freundlich model ($0.95 \leq R^2 \leq 1.00$) characterized the data well over the entire aqueous phase concentration range for each groundwater simulant.
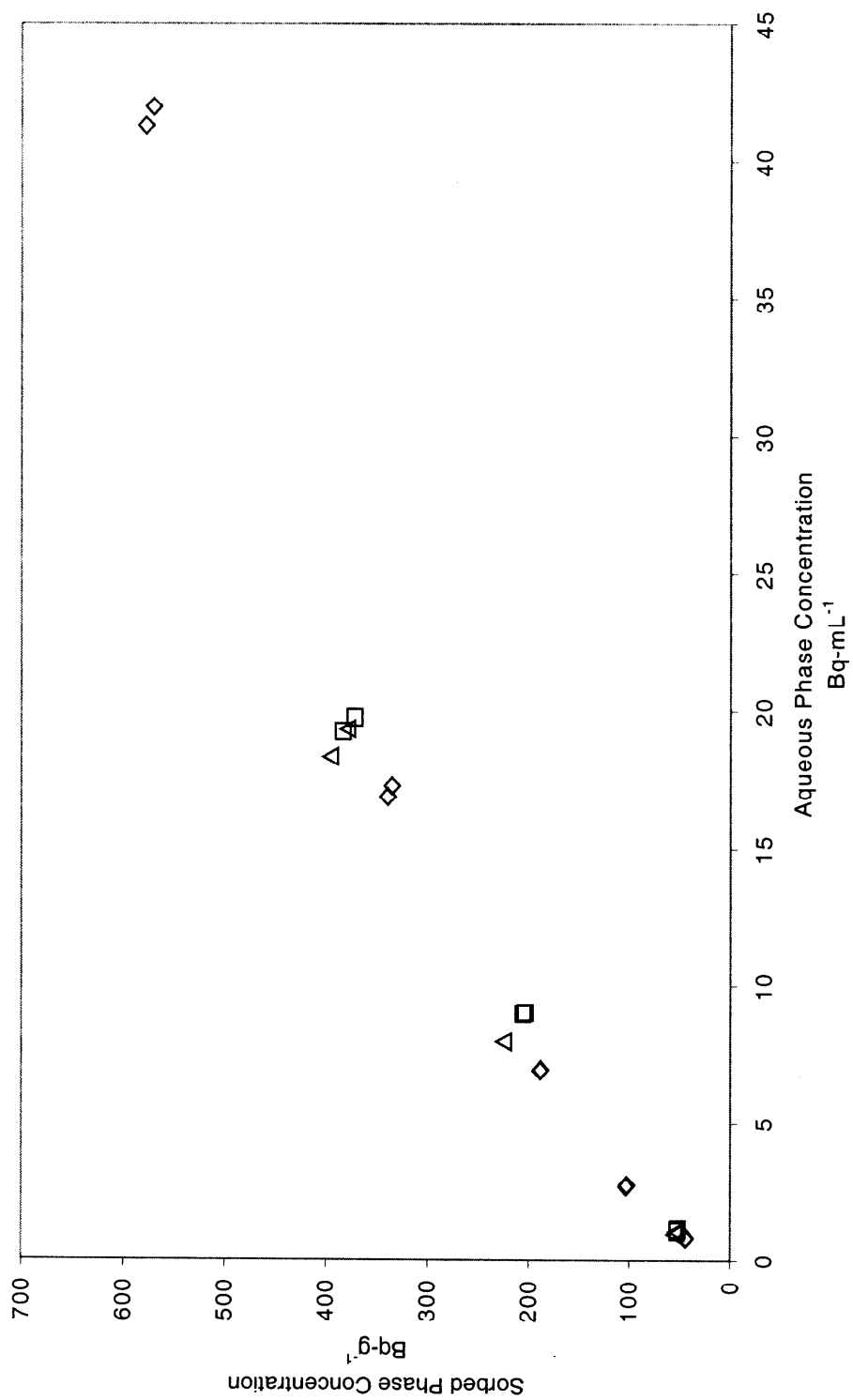
Figure 5.10 Results of ligand study for neptunium on soil I2S-INEEL-105 for GWS (◇); GWS (-CO$_3^{2-}$) (□); GWS (-CO3^{2-}, SO$_4^{2-}$, F$^-$) (△).
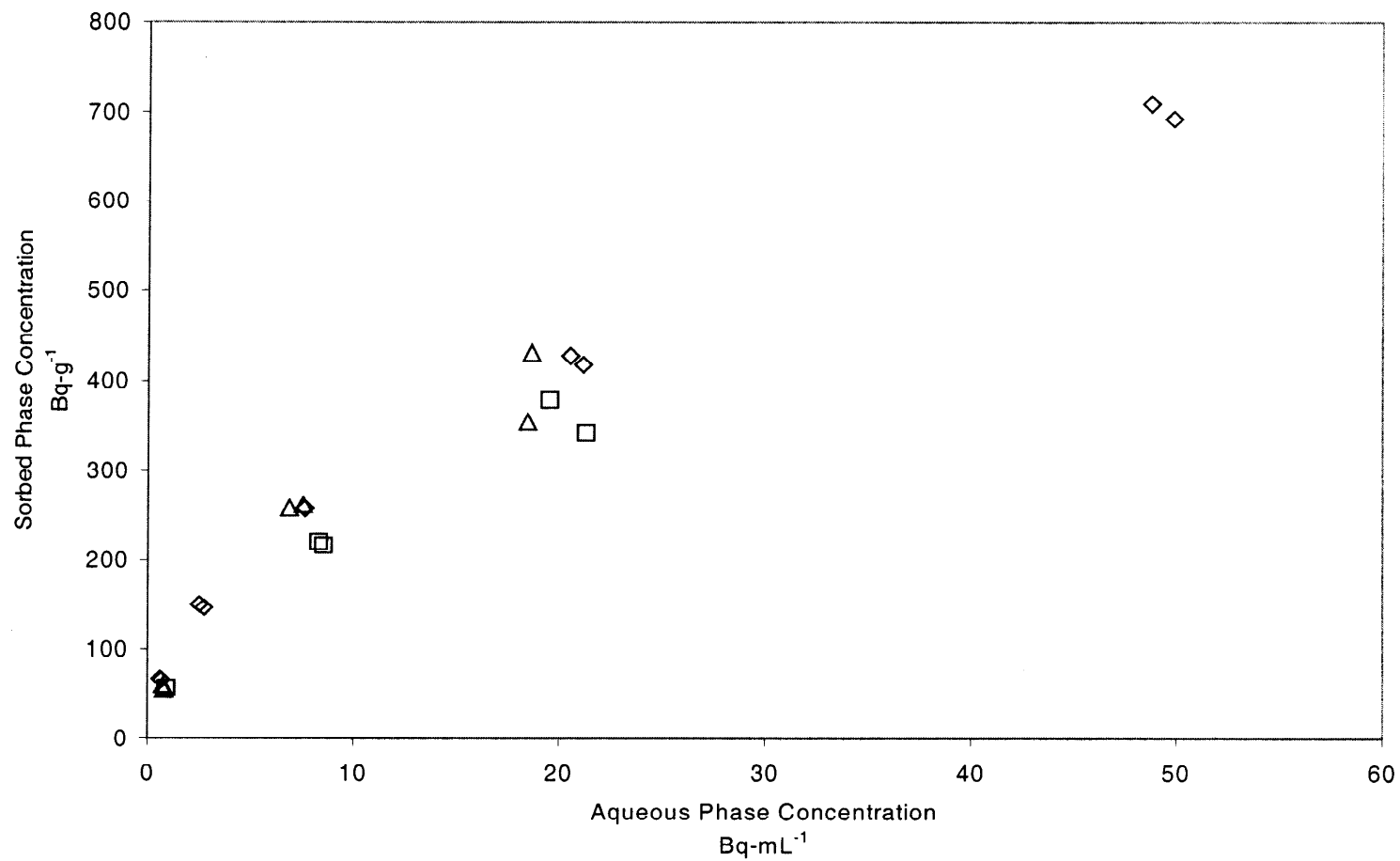
Figure 5.11 Results of ligand study for neptunium on soil I4D-INEEL-234 for GWS (◊); GWS (-CO_3^{2-}) (□);GWS (-$CO3^{2-}$, SO_4^{2-}, F⁻) (Δ).

Table 5.15 Summary of Freundlich parameters with statistics of fit determined from ligand study data for neptunium on soil I2S-INEEL-105 and I4D-INEEL-234.

SIMULANT	I2S-INEEL-105			I4D-INEEL-234		
	K_F[†] $mL^n\text{-}g^{-n}$	n[†]	R^2	K_F[†] $mL^n\text{-}g^{-n}$	n[†]	R^2
GWS	52 ± 0.4	0.65 ± 0.016	1.00	76 ± 2.4	0.60 ± 0.024	0.98
GWS ($-CO_3^{2-}$)	48 ± 1.2	0.68 ± 0.033	1.00	60 ± 2.7	0.60 ± 0.035	1.00
GWS ($-CO_3^{2-}, SO_4^{2-}, F^-$)	51 ± 1.8	0.71 ± 0.071	0.99	71 ± 4.5	0.60 ± 0.14	0.95

[†]Results are reported at ± 95% confidence interval.

A statistical analysis was performed to determine if the partitioning data for each groundwater simulant were significantly different. The results of the analysis of variance indicate that the partitioning data sets were within the 95% confidence interval and not statistically different. This suggests that the variations in groundwater simulant composition caused no difference in neptunium's sorption behavior, which implies that carbonate, sulfate, and fluoride, which varied across the three groundwaters, probably exerted little influence on neptunium sorption. Additionally, neptunium(V) speciation in GWS was determined via MINTEQA2 geochemical code and is presented in Figure 5.12 as percent species of total neptunium vs. pH (Allison *et al.*, 1991). The speciation modeling predicts NpO_2^+ to dominate neptunium speciation below pH 8.5. From pH 8.5 to 9, $NpO_2CO_3^-$ becomes the dominant neptunium species. Above pH 9, $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ become significant. Because these experiments were carried out below pH 8.5 and the data from the ligand studies were statistically similar, the predominant sorbing neptunium species was likely NpO_2^+.
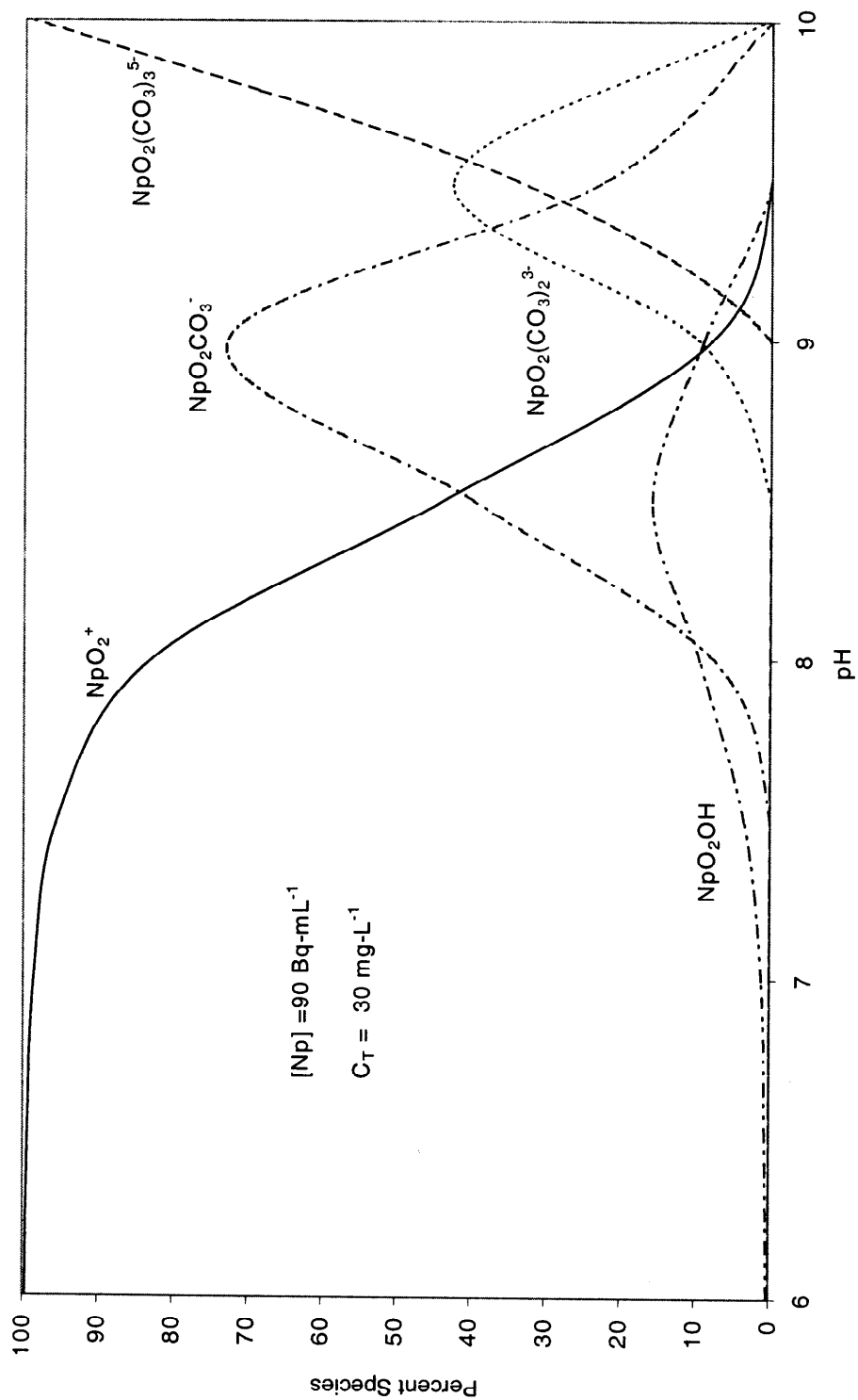
Figure 5.12 Computed speciation of NpO_2^+ as a function of pH in GWS via MINTEQA2 (Allison *et al.*, 1991).